

## **Final Report**

**Contract Number FA2386-09-1-4043**

### **Synthesis of Core-Shell Nanoparticle Composites**

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## **Summary**

In this study hybrid nanoparticles ( $\text{Pd@SiO}_2$ ,  $\text{Au@Gd}_2\text{O}_3$ ) have been synthesized and characterized.  $\text{Gd}_2\text{O}_3\text{:Eu}$  NPs were successfully synthesized using polyol synthetic routes. Nanoparticles with an average diameter size of 1-2 nm were produced in high yield. XPS analysis confirmed the successful coating of the nanoparticles with PEGCOOH and aminocaproic acid.

Palladium nanoparticles synthesized using an aqueous route was more stable in aqueous solvent than palladium nanoparticles synthesized in the investigated polyol route. The coating of palladium nanoparticles with a silica shell was achieved by stirring the nanoparticles in tetraethyl orthosilicate (TEOS).

$\text{Au@Gd}_2\text{O}_3$  nanoparticles were synthesized by stirring monodispersed gold nanoparticles, which were produced from reducing a  $\text{HAuCl}_4$  solution, in a suspension of pre-prepared  $\text{Gd}_2\text{O}_3$  nanoparticles.

## **1. Introduction**

Nanoparticle composites have attracted considerable interest for applications in various areas, such as biomedicine (e.g. cancer diagnosis and treatment, cells labeling), water treatment (removal of pollutants), and manufacturing (plasmon resonant glass coatings, X-ray absorption).

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14. ABSTRACT <b>In this study hybrid nanoparticles (Pd@SiO<sub>2</sub>, Au@Gd<sub>2</sub>O<sub>3</sub>) have been synthesized and characterized. Gd<sub>2</sub>O<sub>3</sub>:Eu NPs were successfully synthesized using polyol synthetic routes. Nanoparticles with an average diameter size of 1-2 nm were produced in high yield. XPS analysis confirmed the successful coating of the nanoparticles with PEGCOOH and aminocaproic acid. Palladium nanoparticles synthesized using an aqueous route was more stable in aqueous solvent than palladium nanoparticles synthesized in the investigated polyol route. The coating of palladium nanoparticles with a silica shell was achieved by stirring the nanoparticles in tetraethyl orthosilicate (TEOS). Au@Gd<sub>2</sub>O<sub>3</sub> nanoparticles were synthesized by stirring monodispersed gold nanoparticles, which were produced from reducing a HAuCl<sub>4</sub> solution, in a suspension of pre-prepared Gd<sub>2</sub>O<sub>3</sub> nanoparticles.</b>					
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In the area of aerospace applications electromagnetic waves absorbing nanoparticle composites in a polymer matrix may provide the platform for novel technologies. Aspects such as interaction of these nanomaterials with especially RADAR waves, waves in the soft X-rays and extreme ultraviolet range of the spectrum, and the so far rarely studied Terahertz radiation have not yet been widely explored, although it is known that nanoparticles of materials such as gold, silver, and magnetite can interact with electromagnetic waves (surface plasmon resonance) in the visible and infrared range of the spectrum. In addition, absorbing properties of nanomaterials in the infrared region of the spectrum have been reported which may provide the base for infrared absorbing materials for applications in heat shielding and stealth technologies.

As a first step towards developing electromagnetic wave absorbing nanomaterials the synthesis of a number of potential materials was studied.

## **2. Synthesis Procedures of Gadolinium oxide nanoparticles**

### **2.1 Materials**

Di(ethylene glycol) (DEG, Sigma, USA), gadolinium (III) chloride hydrate ( $\text{GdCl}_3$ , Aldrich, USA), sodium hydroxide (NaOH, Chem-supply, Australia), poly(ethylene glycol) bis(carboxymethyl)ether (PEG, average Mn ca.600, Aldrich, USA), ethanol (Analytical Reagent, Australia) and Milli Q water.

### **2.2 Gadolinium oxide core**

0.5 g of gadolinium chloride salt was added into 7.5 ml of DEG under vigorous stirring. The solution was heat at  $140^\circ\text{C}$  for 1 h followed by the addition of 0.36 ml 3M NaOH solution. The solution was stirred for another half an hour. Then, the temperature was raised to  $180^\circ\text{C}$  and heated for

another 4 hours.

### **2.3 Larger gadolinium oxide nanoparticles**

0.5 g of gadolinium chloride salt was added into 7.5 ml of DEG under vigorous stirring at 140°C for 1 hour. To the solution, 2.5 ml of gadolinium oxide nanoparticles prepared as above was added. Then, 175µl of 6M NaOH solution was added. The solution was heated at 180°C for 4 hours. 100 mg of PEG was dissolved in 2 ml of DEG and added to the reaction mixture.

### **2.4 Eu/Gd oxide nanoparticles**

A similar procedure was undertaken as the synthesis of gadolinium oxide nanoparticles. Europium inclusions within the Gd<sub>2</sub>O<sub>3</sub> nanoparticles were obtained by adding a small portion (5 to 10 % wt/wt) of europium chloride to the gadolinium chloride solution. Gadolinium chloride solution was kept as 0.2 M with appropriate amount of europium chloride. The solution was heat at 140°C under reflux for 1 h. To a 20 ml of reaction mixture, 1 ml of 3M NaOH solution was added. The solution was stirred and heated at 180°C for another 4 hours.

### **2.5 Purification**

Purification of nanoparticles synthesized as above was performed by dialysis against ethanol. The colloidal solution was introduced in a tubular membrane of cellulose and immersed in 500 ml of ethanol which was replaced every few hours for 2 days. The resulted product was concentrated via a rotary evaporator and stored in ethanol.

### **2.6 Characterization**

The morphology and size were characterized via TEM. The surface

composition of sample was characterized via XPS.

## 2.7 Results and discussion

The particle size was determined by TEM. TEM images show that both  $\text{Gd}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$  and Eu inclusion nanoparticles have a diameter size around 1-2 nm with an apparently narrow size distribution. The surface composition of nanoparticles synthesized was characterized by XPS.

The general survey of gadolinium oxide NPs was shown as below (Figure 1). The XPS peaks show that the particles contain mainly Gd, O, and C. The C element is ascribed to biopolymer coating and the adventitious hydrocarbon from the XPS instrument itself. The binding energies of Gd  $3d_{5/2}$ , O 1s and Gd  $4d_{5/2}$  obtained were 1187, 530 and 150 eV, respectively. All these values are 0.6 to 1 eV lower or higher than the ones found in the literature for the same species –  $\text{Gd}^{3+}$ ,  $\text{O}^{2-}$ . This is a known phenomenon when an external reference is being analyzed, since an important contact potential may exist between inorganic sample and the organic contaminant film.

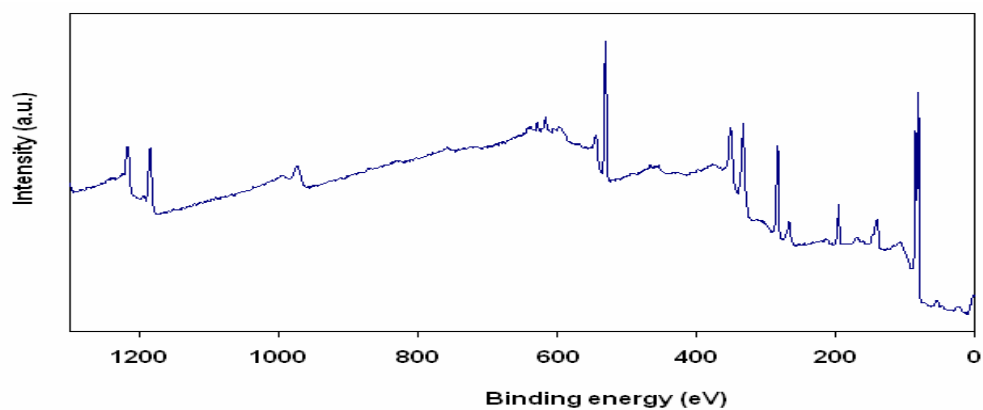
The C 1s peaks displayed doublet asymmetric shape (Figure 1, b), which could be fitted with two components centered at 285 and 286.8 eV. Peak at 286.8 and 285 eV are assigned to the hydrocarbon (C-C, C-H) and the C-O-R of the DEG, respectively. The O 1s peaks displayed asymmetric shape with wider right side as shown in part b of Figure 1, which could be fitted with two components centered at 533.3 and 531.5 eV tentatively assigned to oxide and hydroxyl oxygen chemisorbed on the surface of the sample, respectively. Absorbed water is often present on binary oxides (532eV). Rare earth oxides readily collected water from the air, but do not convert to hydroxide form. That is why they are said to be hygroscopic. High resolution XPS analyses of Gd (3d) level indicated a spin orbit split doublet, with Gd ( $3d_{5/2}$ ) and Gd( $3d_{7/2}$ ) peaks at 1187.8 and 1219.6 eV, respectively.

As each element has its characteristic peak on XPS analysis. Peaks appear at 1154.8 and 1125.23 eV are respectively assigned to be  $3d_{3/2}$  and  $3d_{5/2}$  of Eu. This result is consistent to a reference value, indicating the presence of Eu in the sample. XPS experiments confirm the presence of europium inclusion in gadolinium oxide nanoparticles.

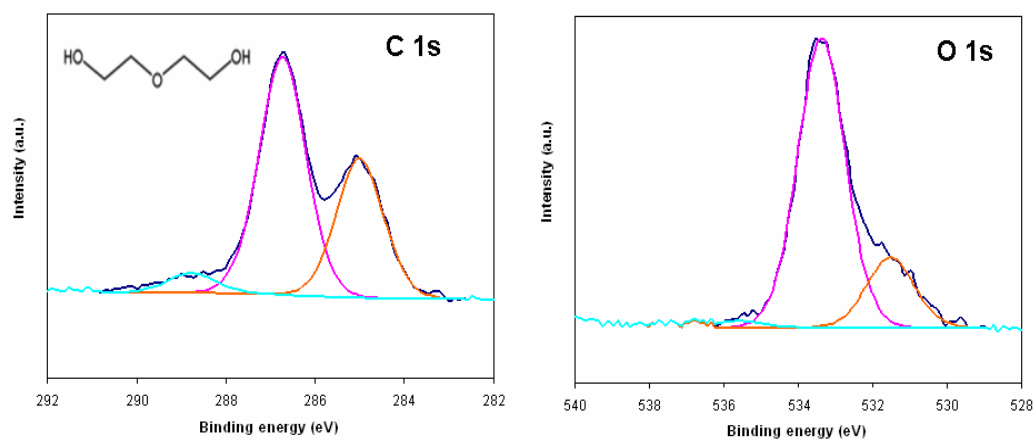
These synthesized nanoparticles were further coated with PEGCOOH600 and amino caproic acid. The successful coating of PEG on particles surface could be determined via XPS analysis. PEGCOOH600 was used, which has a chemical functional group of carboxyl (COOH), carbonyl (C=O), ether group (C-O-R) and hydrocarbon (C-C, C-H). All four chemical groups (Figure 2) were observed at 289.1, 287.6, 286.6 and 285 eV, respectively from the O (1s) spectrum of PEGylated  $Gd_2O_3$  NP XPS analysis, indicating the success coating of PEG on the particles. Similarly, the presence of carboxyl (C=O), hydroxyl (C-OH) and alkane (C-C) were observed at 289, 286.6 and 285 (Figure 3) respectively, indicating the successful coating of aminocaproic acid on these particles.

Time resolved fluorescence analysis of europium inclusion gadolinium oxide nanoparticles give similar result as europium chelated by EDTA (Figure 4). XPS and time resolve fluorescence analysis both confirmed the inclusion of europium.

(a) Gd<sub>2</sub>O<sub>3</sub> NPs in DEG spectrum



(b) C (1s) and O (1s) spectrum



(c) 1,000-1,400 eV spectrum

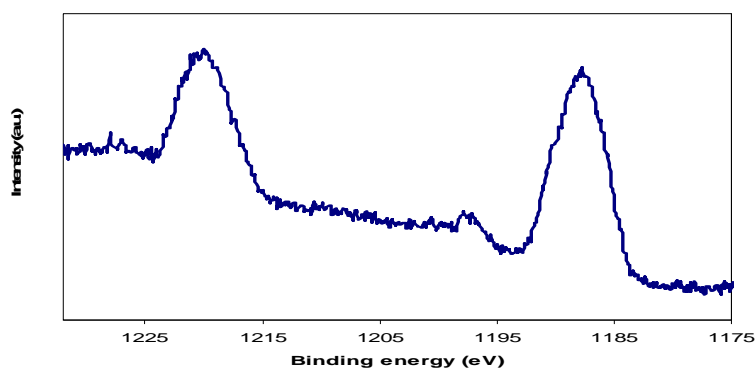
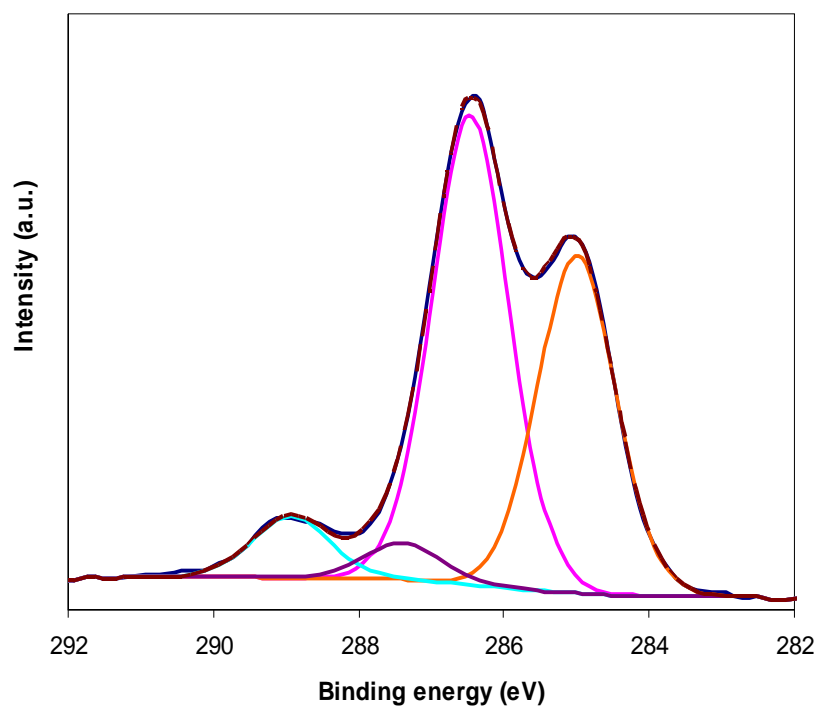


Figure 1 XPS spectra of Gd<sub>2</sub>O<sub>3</sub> NPs (DEG)

(a) C (1s) spectrum



(1s) spectrum

(b) O

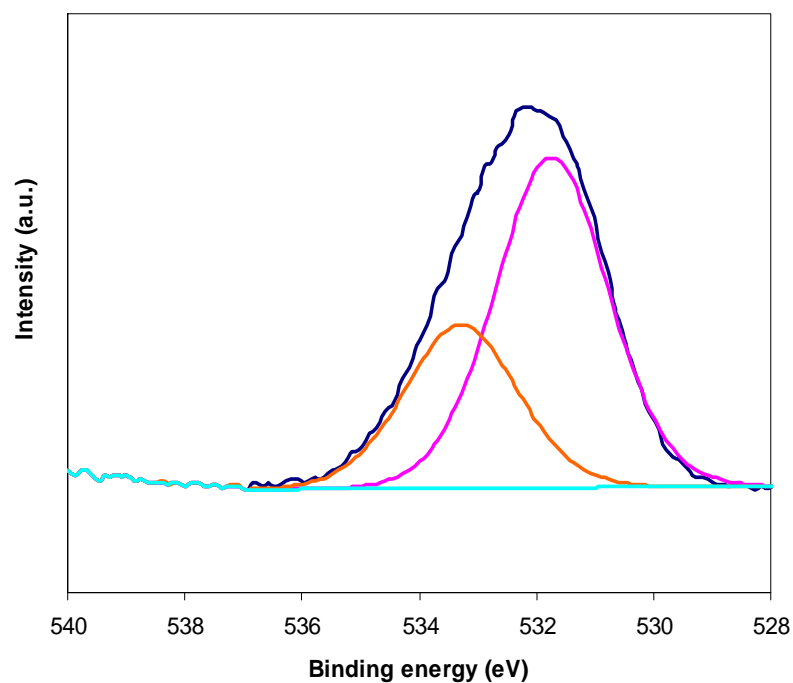
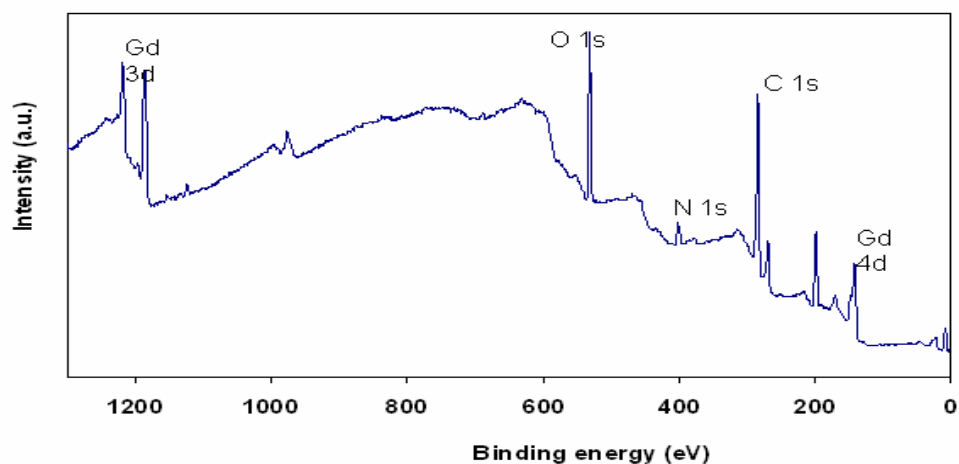


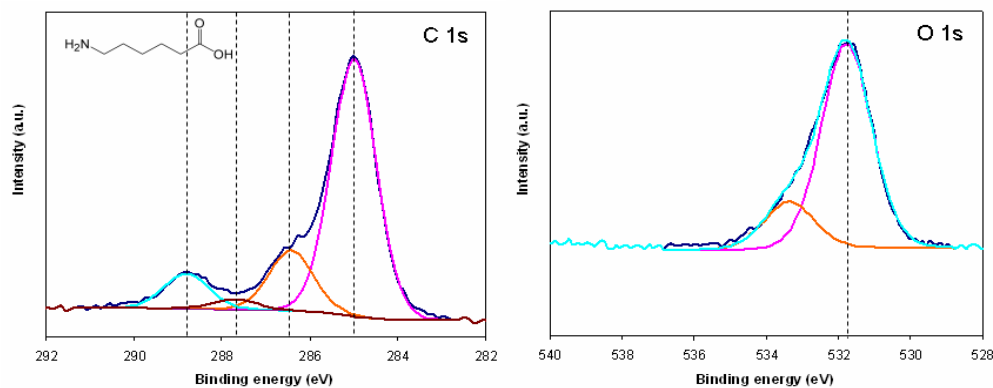
Figure 2 XPS spectra for PEGylated Gd<sub>2</sub>O<sub>3</sub> NPS



(a)  $\text{Gd}_2\text{O}_3$ : Eu nanoparticles coated with Aminocaproic acid spectrum



(b) C (1s) and O (1s) spectrum



(c) 1,000-1,400 eV spectrum

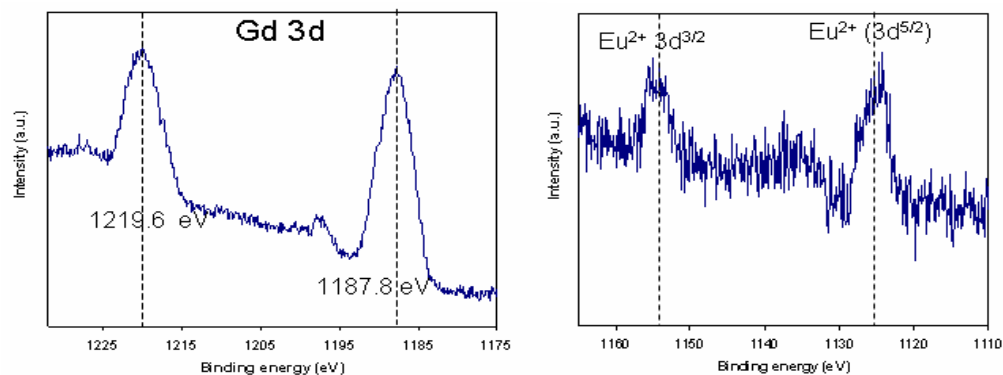


Figure 3 XPS spectra of  $\text{Gd}_2\text{O}_3$ : Eu nanoparticles coated with Aminocaproic acid

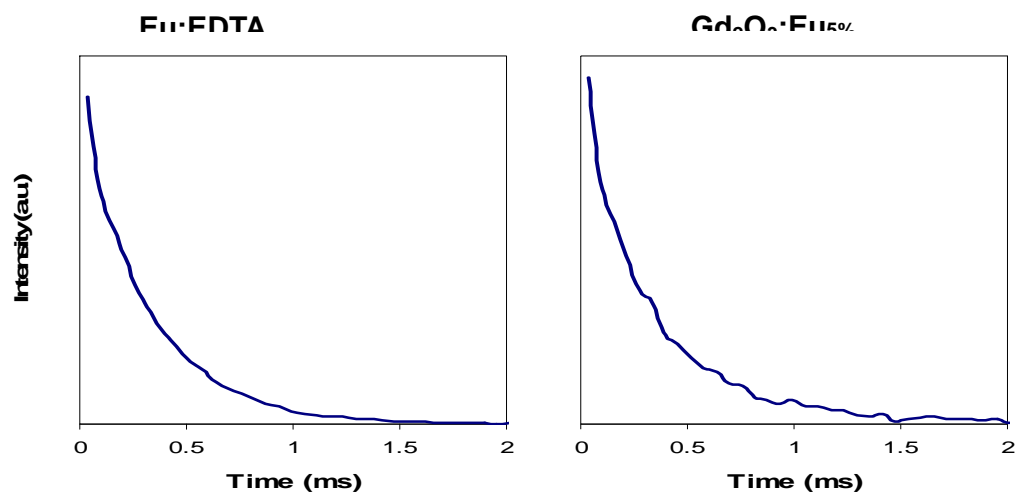


Figure 4 Time fluorescence analysis of Gd<sub>2</sub>O<sub>3</sub>: Eu nanoparticles coated with Aminocaproic acid

**Table 1 Summary of XPS analysis of Eu: Gd<sub>2</sub>O<sub>3</sub> NPs**

Peak ID	Reference BE	Measured BE
Gd 3d <sub>5</sub>	1186.9	1187.8
Gd 3d <sub>3</sub>	1219.6	1219.6
O Gd <sub>2</sub> O <sub>3</sub>	532.5	531.0
Eu 3d <sub>5</sub>	1126	1125.2
Eu 3d <sub>3</sub>	1155	1154.8
C (C-C, C-H)	284.5	285.0-285.1
C (C-OR)	285.4	286.6-286.8
C (C=O)	287.8	287.6
C (COOR)	288.9	289.1

### 3. Synthesis of palladium core nanoparticles

#### 3.1 Materials

Palladium (II) sodium chloride ( $\text{Na}_2\text{PdCl}_4$ , Aldrich, USA), ethylene glycol (EG, Unilab, Australia), Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Chem-Supply, Australia), poly(vinyl) pyrrolidone (PVP, Aldrich, USA, molecular weight = 55000), pluronic F127 (BASF, USA), pluronic P123 (BASF, USA), ethanol (Analytical Reagent, Australia), tetraethyl orthosilicate (TEOS, Fluka, Germany), ammonia 30% solution ( $\text{NH}_4\text{OH}$ , Chem-Supply, Australia), di(ethylene glycol) (DEG, Sigma, USA), Gadolinium (III) chloride hydrate ( $\text{GdCl}_3$ , Aldrich, USA), sodium hydroxide ( $\text{NaOH}$ , Chem-supply, Australia) and Milli Q water.

#### 3.2 Organic-phase synthesis

PVP was used as surfactant and  $\text{Na}_2\text{PdCl}_4$  was used as the palladium precursor. 0.001g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved with 5 ml of EG in a double-neck flask at a  $90^\circ\text{C}$  oil bath in air under reflux and magnetic stirring for 1 hour.  $\text{FeCl}_3$  was used as an oxidative etchant to control the size of the nanocrystals. 0.0312g of PVP was dissolved in 3 ml of EG with sonication. 0.0162g of  $\text{Na}_2\text{PdCl}_4$  was dissolved in 3 ml of EG, a brownish solution. These two solutions were then pipetted drop by drop into the flask and further mixing at  $90^\circ\text{C}$  for 3 hours. The color of the solution changed from brown to black, indicating the formation of palladium nanoparticles. The use of Pluronic F127 was investigated as an alternative to PVP. A different amount of PVP and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were investigated to increase the stability of palladium nanoparticles in water. 0.4 ml of synthesis mixture with 0.6 ml of ethanol was sonicated to mix. The solution was centrifuged for 20 minutes at a speed of 14000rpm to precipitate the solid. The colorless supernatant was discarded. The resulting solid residual was redispersed in 1 ml of ethanol and centrifuged again. This procedure was repeated three times for further purification. Finally the solid residue was

redispersed in a suitable volume of ethanol or Milli Q water depending on the quantity of the residue.

### **3.3 Aqueous-phase synthesis**

Pluronic P123 was used as surfactant and  $\text{Na}_2\text{PdCl}_4$  was used as the palladium precursor. 0.2 g of pluronic P123 was dissolved with 10 ml of Milli Q water. To the solution, 0.1 ml of 0.1M  $\text{Na}_2\text{PdCl}_4$  solution was added under vigorous stirring and kept stirring overnight. The color of the solution changed within few minutes from bright yellow to a deep brown, indicating the formation of nanoparticles. 1 ml of the final synthesis solution was centrifuged for 4 hours at a speed of 14000rpm to precipitate the solid. The light brownish supernatant was discarded. The resulting solid residual was washed gently with water three times. Finally the solid residue was redispersed in a suitable volume of ethanol or Milli Q water or DEG depending on the quantity of the residue and the use of the particles.

### **3.4 Silica encapsulation**

Palladium nanoparticles were encapsulated with silica using a standard Stöber method. A process hydrolyses TEOS onto the palladium nanoparticles in an ethanol solution containing water and ammonia. Palladium nanoparticles dispersed in ethanol were first prepared. To 0.6 ml of palladium nanoparticles solution, 5 ml of ethanol and 10  $\mu\text{l}$  of TEOS were added. The reaction mixture was sonicated and 0.5 ml of ammonia was added under sonication. The reaction mixture were further sonicated for 5 minutes and stirred at room temperature over night. The palladium core silica shell suspension was centrifugally separated from the suspension and washed with ethanol 3 times. Finally the solid residue was redispersed in a suitable volume of Milli Q water depending on the quantity of the residue.

### **3.5 Characterization**

The morphology and size of the synthesized particles were characterized using Transmission Electron Microscopy (TEM). The surface composition of hybrid particles was characterized using X-ray Photoelectron Microscopy (XPS).

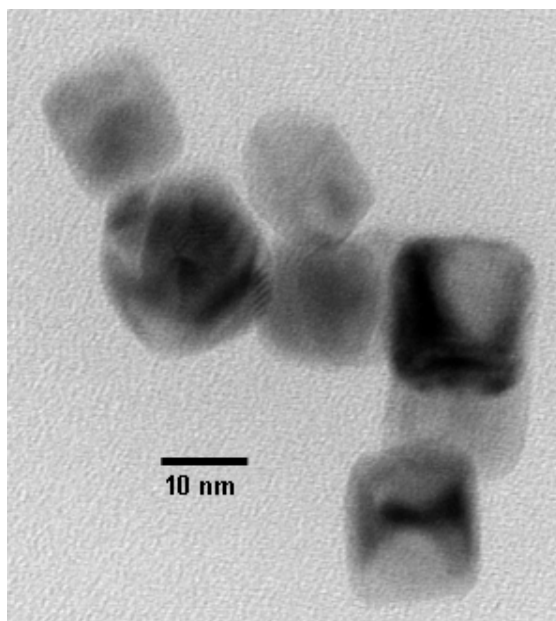
### **3.6 Results and Discussion**

Two synthesis methods, organic-phase and aqueous-phase, were used in this study. Palladium nanoparticles synthesized via organic-phase show slightly truncated nanocubes in shape with an average width of 15 nm as shown by TEM image (Figure 5). The particles size can be adjusted by varying the initial metal ion concentration. The oxidative etching of palladium seeds by  $\text{Fe}^{3+}$  could reduce the number of seeds formed in the nucleation step. As the number of seeds decrease, larger nanocubes form. However, these palladium nanoparticles are not stable in aqueous solvent. Thus, aqueous-phase method was used. Palladium nanoparticles synthesized through this method are spherical shape and have an average diameter size of 7 nm, as shown by TEM image (Figure 6). These synthesized particles are stable in aqueous solvent. As expected, palladium nanoparticles synthesized via polyol reduction with  $\text{FeCl}_3$  as etching agent are larger. The nucleation rate of the particles was directly related to synthesis temperature. The high temperature ( $90^\circ\text{C}$ ) employed in the polyol reduction method; appear to increase the kinetic of the reaction that forms the particles. Aqueous-phase synthesis at room temperature grows smaller nanoparticles.

The surface composition of the synthesized nanoparticles was characterized by XPS. The general survey of palladium nanoparticles was shown as below (Figure 7). The most intense peak is 334.5/340.1 eV due to emission from the 3d levels of the Pd atoms, while the 3p and 3s levels give rise to peaks at 534/561 eV and 673 eV, respectively. The absence of

the Pd 3d peak might indicate the successful coating of silica on the palladium nanoparticles (Figure 8). Peaks at 150.5 and 100.1 eV were observed, which are assigned to 2s and 2p of silica respectively, indicating the presence of silica. This is further confirmed with TEM analysis. TEM analysis of silica coated palladium nanoparticles solution shows the formation of a bright shell around the palladium nanoparticles which is believed to be silica (Figure 9).

(a) TEM image



(b) Size distribution

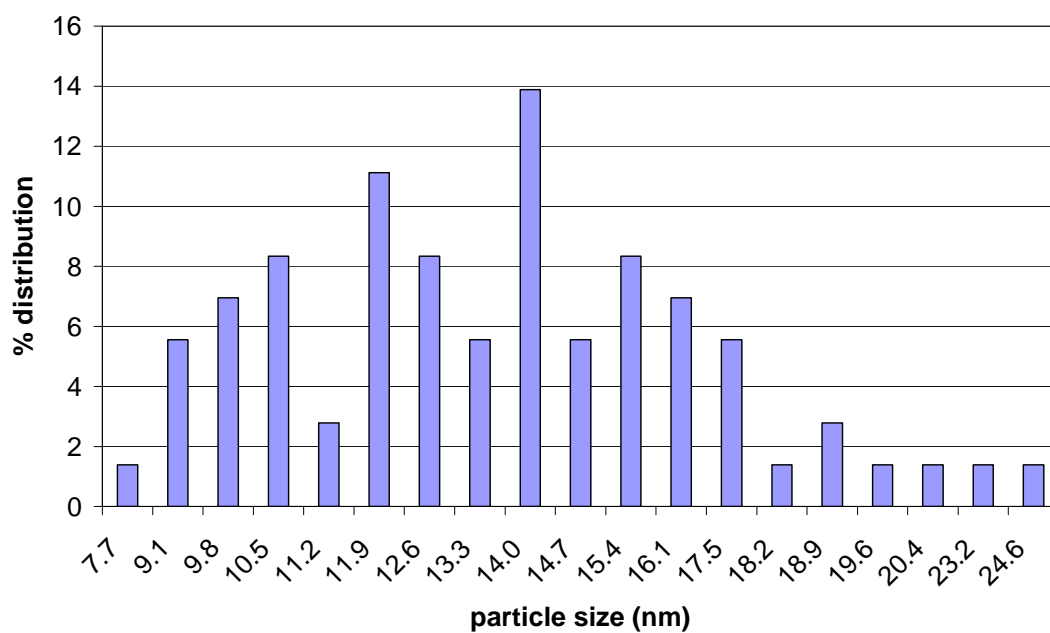
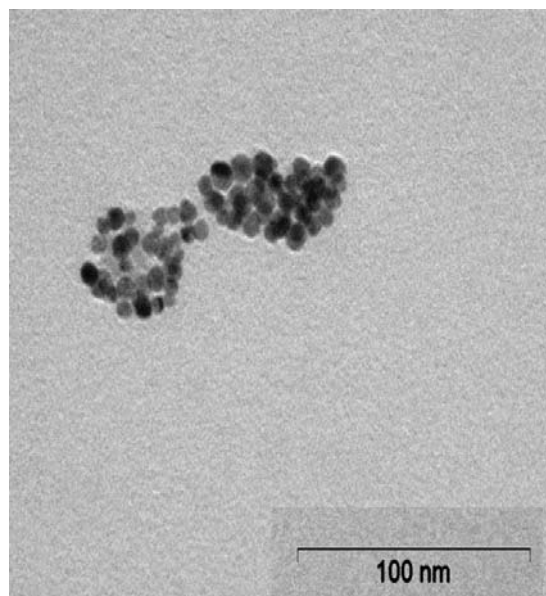


Figure 5 (a) TEM image and (b) size distribution of organic-phase



synthesis Pd NPs. Based on the analysis of 75 particles on TEM images

(a) TEM image



(b) Size distribution

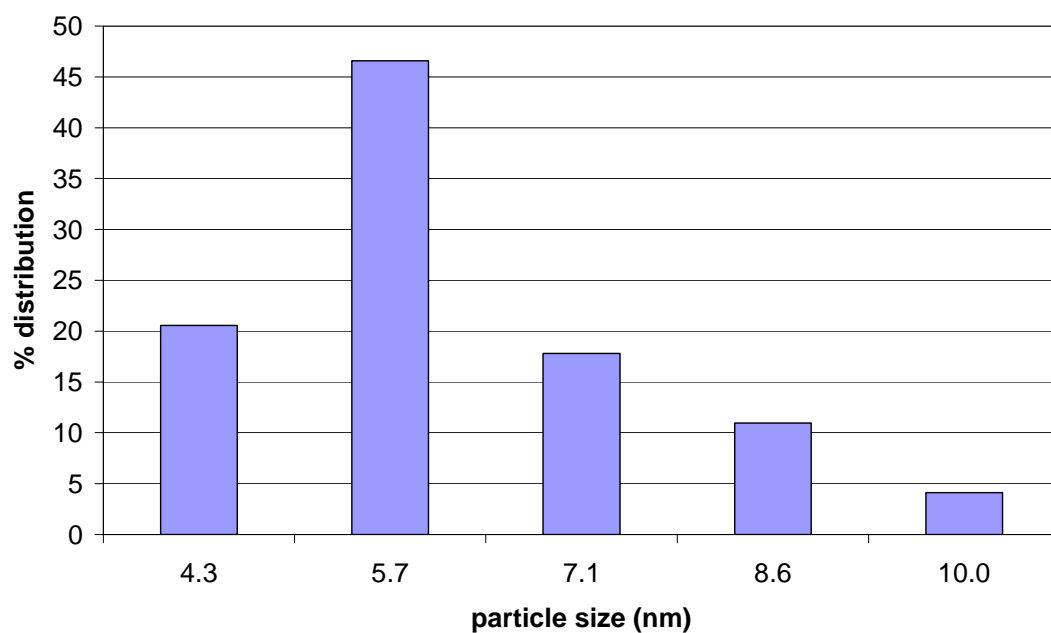
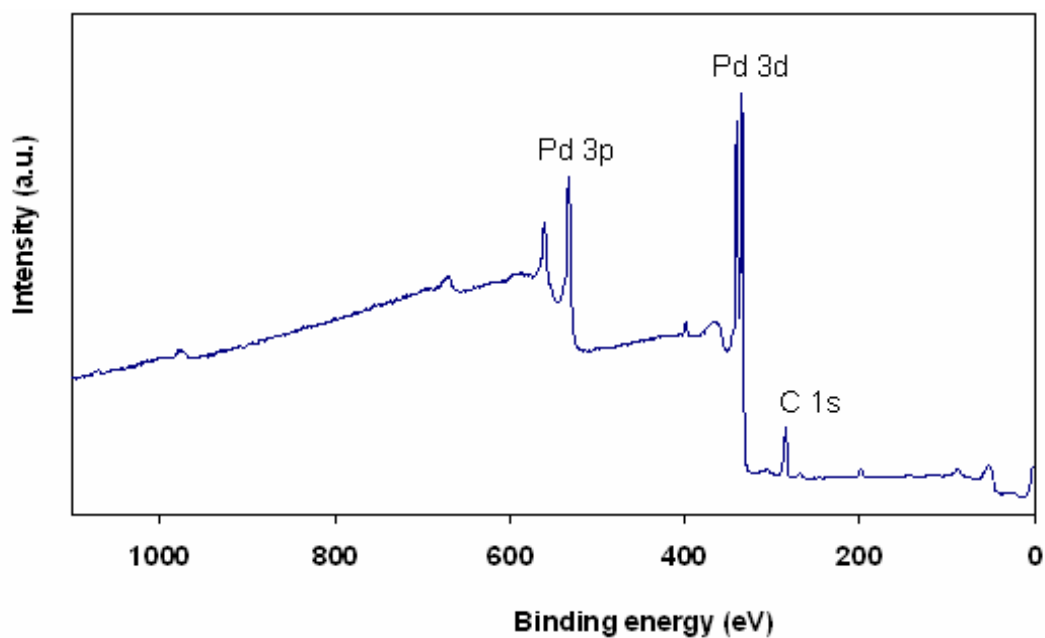


Figure 6 (a) TEM image and (b) size distribution of aqueous-phase synthesis Pd NPs. Based on the analysis of 75 particles on TEM images.

(a) Palladium nanoparticles spectra



(b) High resolution of 3d orbital of palladium NPs

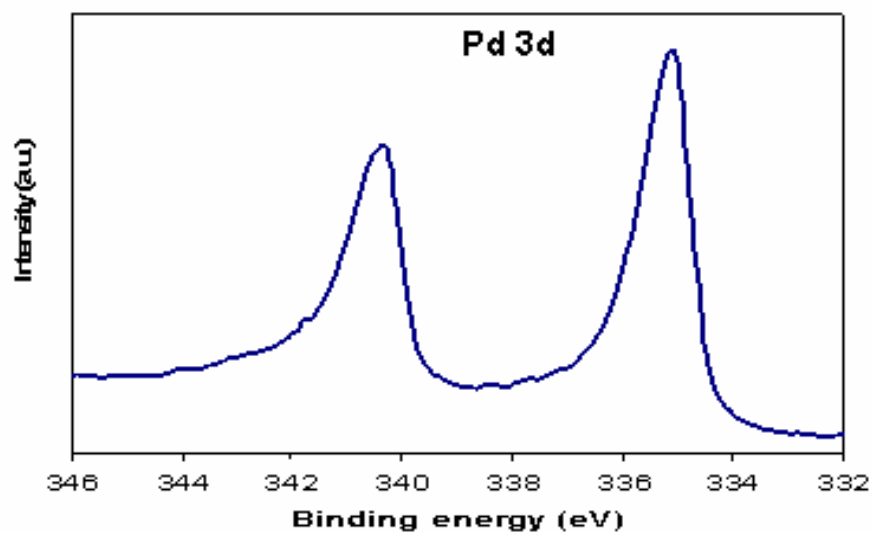


Figure 7 XPS images of palladium nanoparticles

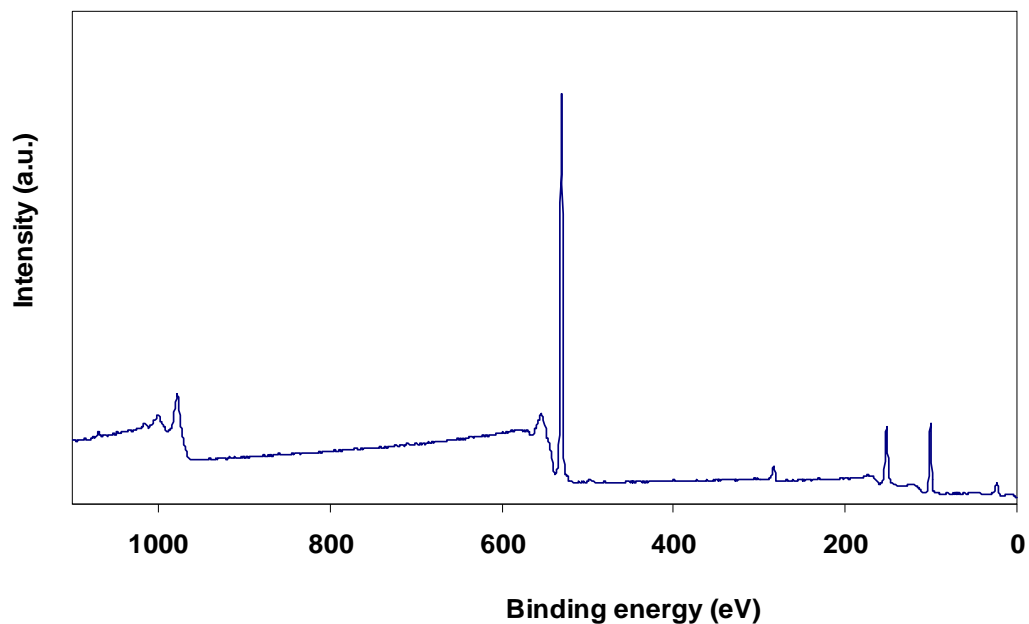


Figure 8 XPS image of silica coated palladium nanoparticles

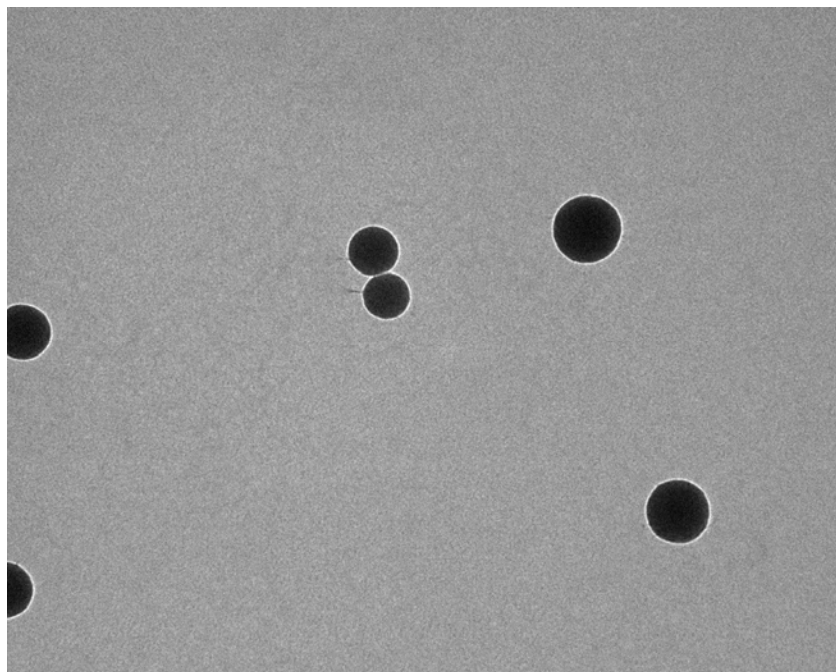


Figure 9 TEM image of silica coated palladium nanoparticles

**Table 2      Summary of XPS analysis of Pd NPs**

<b>Peaks ID</b>	<b>Reference BE</b>	<b>Measured BE</b>
Pd 4d	1.4	1
Pd 4p	50.7	52
Pd 4s	88.2	87.5
Pd 3d5	335.0	334.5
Pd 3d3	340.3	340.1
Pd 3p3	532.3	531
Pd 3p1	560.0	557.5
Pd 3s	671.5	667.5
Si 2p	100.1	100
Si 2s	150.5	148.15

## **4. Synthesis of gold core – gadolinium shell nanoparticles**

### **4.1 Materials**

Chloroauric acid, ( $\text{HAuCl}_4$ , Aldrich, USA), tri-sodium citrate (Univar, Australia), di(ethylene glycol) (DEG, Sigma, USA), Gadolinium (III) chloride hydrate ( $\text{GdCl}_3$ , Aldrich, USA), sodium hydroxide ( $\text{NaOH}$ , Chem-supply, Australia), poly(vinyl) pyrrolidone (PVP, Aldrich, USA, molecular weight = 55000), ethanol (Analytical Reagent, Australia) and Milli Q water.

### **4.2 Gold core**

$\text{HAuCl}_4$  was used as the gold precursor and tri-sodium citrate was used as a reducing agents. 150 ml of 0.02M of  $\text{HAuCl}_4$  solution was prepared. The solution was stirred and heat to boil. To the boiled solution, 5.25 ml of 0.34M tri-sodium citrate solution was added. The original yellow solution turn clear as the tri-sodium citrate removes the  $\text{Cl}^-$  ions from the  $\text{Au}^{3+}$  ions. The solution was stirred for another 1 hour. With the increasing size of the gold nanoparticles, the color of the mixture changes from clear to dark blue to wine-red, according to the optical properties of the particles. The gold nanoparticles gradually formed as the citrate reduced the gold (III) growing to monodisperse spherical particles. While the remaining  $\text{Cl}^-$  and  $\text{Na}^+$  ions remain in the colloidal dispersion, the citrate molecules act as a negatively charged coating of gold nanoparticles. The resulting repulsive forces between the gold nanoparticles stabilize the suspension and keep the particles from settling down. The solution was centrifuged for 30 minutes at a speed of 14000rpm to precipitate the solid. The colorless supernatant was discarded. Finally the solid residue was redispersed in 0.6 ml of ethanol or DEG.

### **43 Gadolinium oxide shell**

The gold nanoparticles synthesized as above were stabilized by PVP. 0.1g of PVP was dissolved in 2 ml of DEG. To the solution, 7.2 ml of gold nanoparticles in DEG was added and heat at 100°C for 1 hour with vigorous stirring. 5 mg of  $\text{GdCl}_3$  was dissolved in 2 ml of DEG and added to the solution. Then, 20  $\mu\text{l}$  of 6 M NaOH solution was added and heat at 180°C for 1 hour. 0.4 ml of the synthesized mixture was mixed with 1ml of ethanol and for 30 minutes at a speed of 14000rpm to precipitate the solid. The colorless supernatant was discarded. The resulting solid residual was washed with ethanol three times. Finally the solid residue was redispersed in a 0.3 ml of ethanol.

#### **4.4 Characterization**

The synthesized nanoparticles were characterized via TEM. Surface composition of the sample was characterized via XPS.

#### **4.5 Results and discussion**

The colloidal Au NPs was prepared through the reduction of  $\text{Au}^{3+}$  ions to metallic  $\text{Au}^0$  in aqueous media containing tri-sodium citrate. Citrate works as a reducing agent and stabilizing agent. The Au NPs were further coated with  $\text{Gd}_2\text{O}_3$  using the common polyol method. The synthesized Au NPs particle has an average diameter size of 19 nm, based on analysis of 30 particles on TEM images (Figure 10).

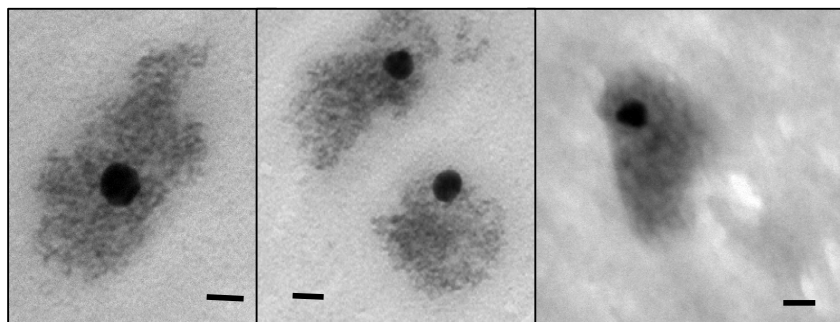
Composition of the grown nanoparticles was analyzed by XPS. The most important characteristics of nanoparticles can be deduced from the presence of Gd (3d) and absence of Au (4f) (Figure 11). Peak appears at 84.4 eV corresponding to the 4f level of gold, indicating the light amount of gold presence on the sample. The encapsulation of  $\text{Gd}_2\text{O}_3$  was suggested by the detection of Gd 3d at 1187.1/1219 eV.

The O 1s peaks displayed asymmetric shape with wider left side as shown in Figure 26. It could be fitted with two components centered at 531.4 and 533 eV tentatively assigned to oxide and hydroxyl oxygen chemisorbed on the surface of the sample. Rare earth oxides readily collected water from the air, but do not convert to hydroxide form. As mention before, citrate was coated on the particles surface as stabilizing agent and to prevent agglomeration. Citrate has chemical functional group of carboxyl (COO), carbonyl (C=O), hydroxyl (C-OH), and alkane (C-C, C-H). These four chemical groups were observed at 289.5, 288.2, 286.4 and 285 eV, respectively.

The XPS analysis suggested large portion of Au NPs was coated with  $Gd_2O_3$  or the particles is not well coated by  $Gd_2O_3$ . The detection of Gd and Au with high resolution TEM analysis further confirmed the presence of  $Gd_2O_3$  on Au surface (Figure 12). The particles were further coated with citrate. TEM images confirmed that Au NPs was not evenly coated by  $Gd_2O_3$ .

Gold NPS displayed a small surface plasmon band centered on 520 nm in UV-vis spectra (Figure 13). This absorption band is assigned to a wave-like motion of electron on the surface of gold NPs. The surface plasmon absorption maximum of gadolinium oxide coated red ship by 6 nm. This red shift is due to the change in the dielectric constant of the medium around gold nanoparticles. Gadolinium oxide coating changed the local environment and thus the surface Plasmon absorption of the nanoparticles is changed. The sharp and narrowed peak indicated no agglomeration. A colour change can be observed from light red to dark red wine after coating with gadolinium oxide (Figure 14).

(a) TEM image



(b) Size distribution

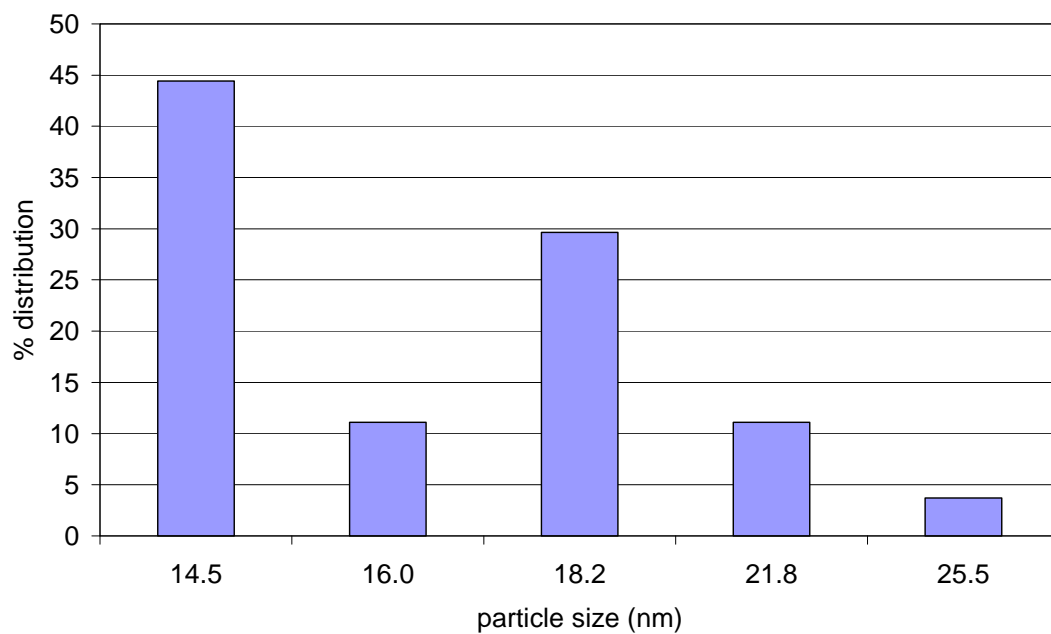
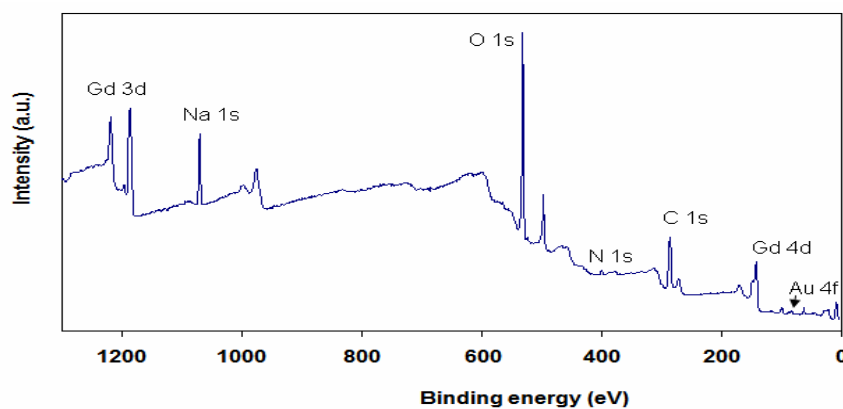


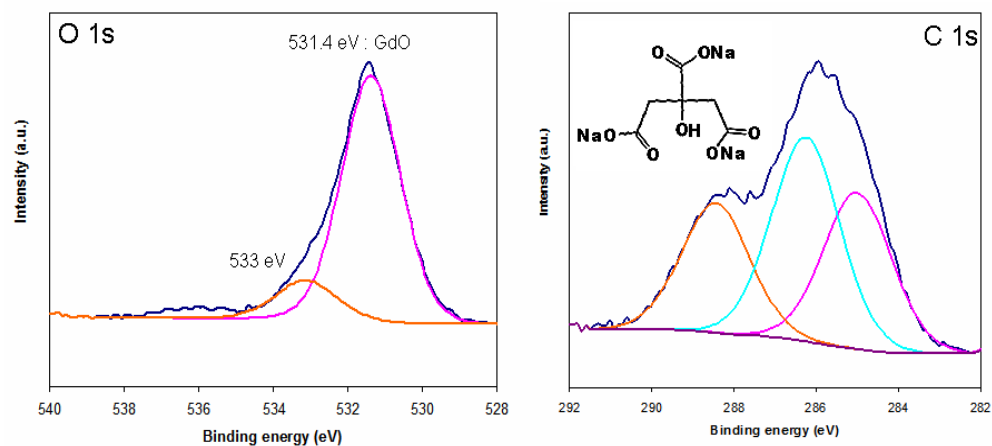
Figure 10 TEM image and size distribution of Au-Gd<sub>2</sub>O<sub>3</sub> NPs. Based on the analysis of 30 particles on the TEM images.



(a) gold-gadolinium oxide core-shell NPs spectrum



(b) O 1s and C 1s spectrum



(c) High resolution spectrum of 3d gadolinium

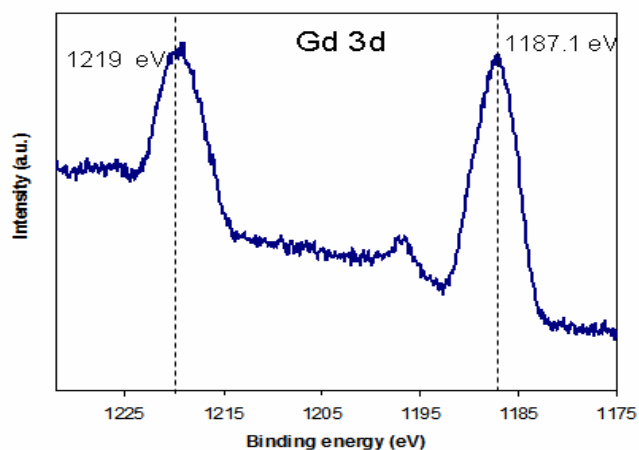


Figure 11 XPS analysis of Au-Gd<sub>2</sub>O<sub>3</sub> NPs

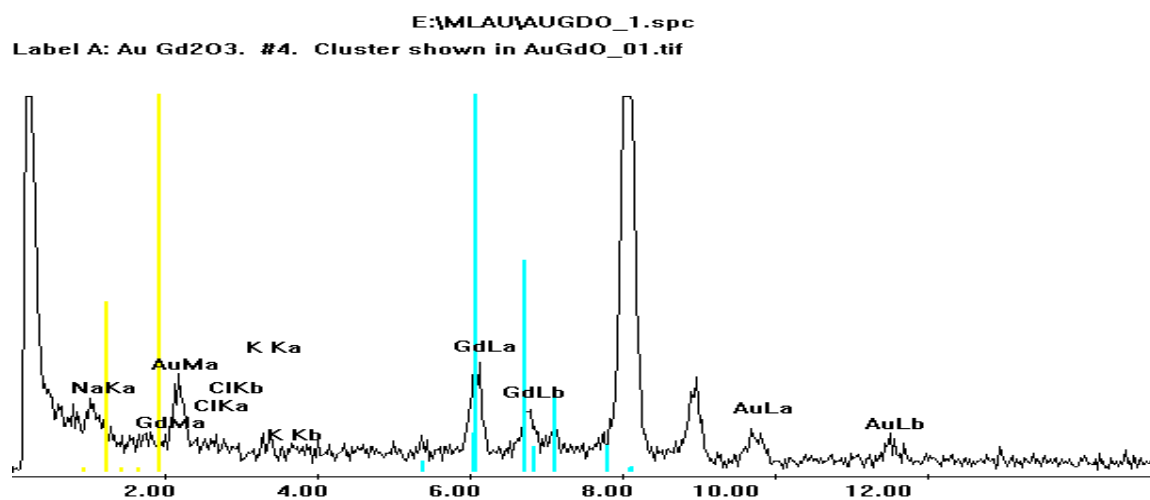


Figure 12 High resolution TEM analysis of Au-Gd<sub>2</sub>O<sub>3</sub> NPs

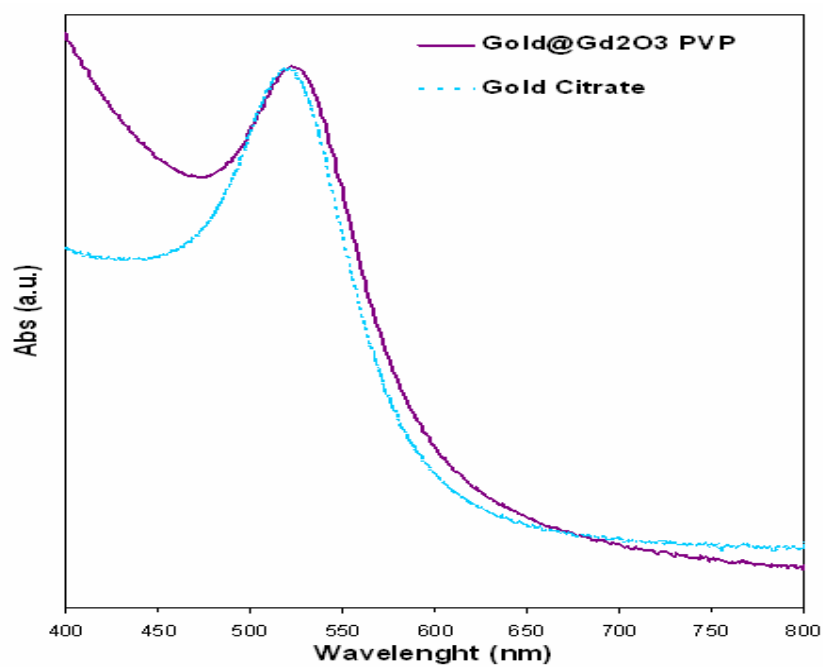


Figure 13 UV-vis spectra of gold NP coated with citrate and gold-gadolinium oxide core-shell nanoparticles.

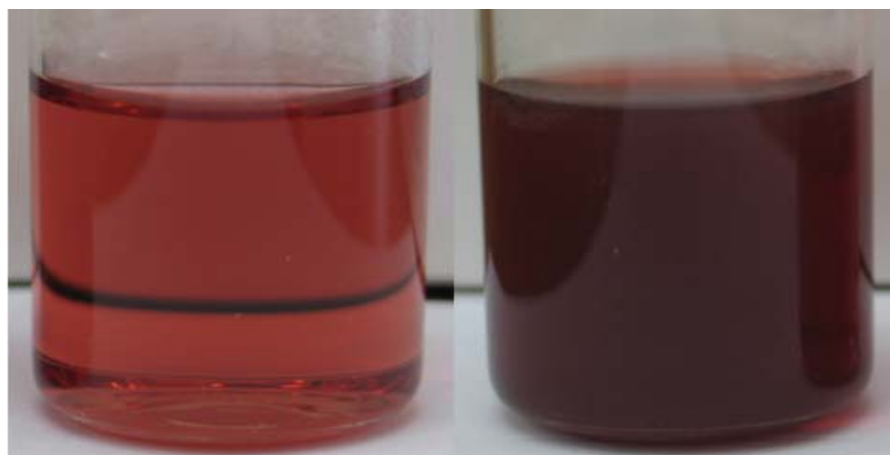


Figure 14 Gold nanoparticles solution before (left) and after (right) coating.



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**Table 3 Summary of XPS analysis of Au@Gd<sub>2</sub>O<sub>3</sub> NPs**

Peak ID	Reference BE (eV)	Measured BE (eV)
Au 4f	85	82.8
Gd 4d5	140.3	141.8
Gd 3d5	1186.9	1187.1
Gd 3d3	1219.6	1219.0
O Gd <sub>2</sub> O <sub>3</sub>	531.1	531
C (C-C, C-H)	284.5	285
C (C-OH)	285.4	286.4
C (C=O)	287.8	288.2
C (COOR)	288.9	289.5